



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 279/02, 287/00	A1	(11) International Publication Number: WO 99/09081 (43) International Publication Date: 25 February 1999 (25.02.99)
(21) International Application Number: PCT/US98/16501 (22) International Filing Date: 7 August 1998 (07.08.98) (30) Priority Data: 60/055,508 13 August 1997 (13.08.97) US (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Mid- land, MI 48674 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): DEMIRORS, Mehmet [TR/US]; 5015 Redfern Circle, Midland, MI 48642 (US). (74) Agent: ZETTLER, Lynn, M.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HIGH GLOSS HIGH IMPACT MONOVINYLDENE AROMATIC POLYMERS (57) Abstract The present invention is a rubber modified monovinylidene aromatic polymer having a bimodal particle size distribution comprising: a) rubber particles of a star or branched low viscosity rubber having a volume average particle size of from 0.1 to 1.5 μ , and a cellular or core shell morphology or mixture thereof, and b) rubber particles of a star or branched low viscosity rubber, linear diene rubber or block copolymer rubber having a volume average particle size of from 1.5 to 10 μ , and a cellular morphology, with the proviso that when the volume average particle size of the particles of a) is greater than 1 μ , the volume average particle size of the particles of b) is at least 2 μ , wherein the particles of a) are from 50 to 99 wt. percent of the total diene rubber content.		

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

HIGH GLOSS HIGH IMPACT MONOVINYLIDENE AROMATIC POLYMERS

The present invention relates to rubber modified monovinylidene aromatic polymers, particularly polymers containing two distinct rubber volume average particle sizes, herein referred to as bimodal compositions.

5 Rubber modified monovinylidene aromatic polymers have typically been prepared from vinyl aromatic monomers by polymerizing the vinyl aromatic monomer in the presence of a dissolved rubber. The vinyl aromatic monomer polymerizes, forming a discontinuous phase dispersed throughout a continuous phase of dissolved rubber in monomer. As the vinyl aromatic monomer continues to polymerize, the discontinuous
10 polymer phase becomes larger in volume, thus forming a continuous phase, while the rubber forms a discontinuous phase dispersed throughout. This phenomenon, referred to as "phase inversion", is, therefore, the conversion of the polymer from a discontinuous phase dispersed in the continuous phase of the rubber/monomer solution, through the point where there is no distinct continuous or discontinuous
15 phase in the polymerization mixture, to a continuous polymer phase having the rubber dispersed throughout.

Various bimodal compositions containing two distinct rubber particle sizes have been produced to attempt to effectively balance and achieve high gloss, while maintaining high impact properties using several types of rubbers. U.S. 4,334,039
20 issued to Dupree et al. and U.S. 4,153,645 issued to Lanza et al. disclose the use of butadiene rubbers to obtain polymers having a bimodal rubber particle size distribution. Such polymers, while having good toughness, do not have the desired level of gloss. EP-048,389 by Echte discloses the use of styrene/butadiene block copolymer rubbers wherein small particles are made from a 40/60 styrene/butadiene block copolymer and
25 are of core-shell type morphology. While such products have the desired balance of gloss and impact, they are economically disadvantageous because of higher cost due to the use of the block copolymer rubbers. Additionally, higher amounts of block copolymer must be used in order to obtain a given polybutadiene level, additionally increasing cost.

30 It is well known in the art that the balance of gloss and impact properties of high impact monovinylidene aromatic polymers is dependent on rubber particle size, rubber level and flow properties of the product. Typically, smaller particle containing resins have higher gloss and lower impact, while larger rubber particle containing resins have lower gloss and higher impact properties. Standard rubbers, usually known as
35 butadiene homopolymer type, cannot be sized small enough to make the desired high gloss products. Block copolymers usually lead to small rubber particles but are more expensive. Other approaches have been used to solve the problem of obtaining small particles using polybutadiene rubbers. EP-277,687 discloses a rubber modified polymer

containing radial or branched polybutadiene rubber having volume average diameter of 0.1 to 1.2 microns (μ) and rubber particles containing either radial, branched or linear rubber having a volume average particle diameter of from 1 to 5 μ . However, while these compositions have high gloss, they do not have sufficient toughness.

5 Therefore, there remains a need to produce rubber modified monovinylidene aromatic polymers having gloss and impact properties similar to those products which use block copolymer rubbers, but without the high cost of block copolymer rubbers.

The present invention is a rubber modified monovinylidene aromatic polymer having a bimodal particle size distribution comprising:

- 10 a) rubber particles of a star or branched low viscosity rubber having a volume average particle size of from 0.1 to 1.5 μ , and a cellular or core shell morphology or mixture thereof, and
- b) rubber particles of a star or branched low viscosity rubber, linear diene rubber or block copolymer rubber having a volume average
- 15 particle size of from 1.5 to 10 microns, and a cellular morphology, with the proviso that when the volume average particle size of the particles of a) is greater than 1 μ , the volume average particle size of the particles of b) is at least 2 μ ,
- wherein the particles of a) are from 50 to 99 wt. percent of the total diene

20 rubber content.

The polymers of the present invention have excellent gloss and impact properties similar to those obtained using block copolymer rubbers, while being more economical. Such products are highly desirable in replacing higher cost products in injection molding and extrusion applications.

25 The present invention is related to rubber modified monovinylidene aromatic polymers. The monovinylidene aromatic rubber modified polymers are derived from one or more vinyl aromatic monomers. Representative vinyl aromatic monomers include styrene, alkyl substituted styrenes such as alpha-alkyl-styrenes, for example alpha-methylstyrene, alpha-ethylstyrene; ring substituted styrenes, for example,

30 vinyltoluene, particularly p-vinyltoluene, o-ethylstyrene and 2,4-dimethylstyrene; ring substituted halo-styrenes such as chlorostyrene, and 2,4-dichloro-styrene; styrene substituted with both halo and alkyl groups, such as 2-chloro-4-methylstyrene, vinyl anthracene; and mixtures thereof. Preferably styrene and/or alpha-methylstyrene is used as the vinyl aromatic monomer, with styrene being most preferred.

35 Comonomers may also be used in combination with the vinyl aromatic monomer, preferably in an amount of up to 40 percent by weight of the polymerizable monomer mixture. Representative comonomers include unsaturated nitriles, such as acrylonitrile; alkyl acrylates and alkyl methacrylates such as methyl methacrylate or n-

butylacrylate; ethylenically unsaturated carboxylic acids; and ethylenically unsaturated carboxylic acid derivatives including anhydrides and imides, such as maleic anhydride and N-phenyl maleimide.

5 The rubber suitable for use to produce rubber particles having a volume average particles size of from 0.1 to 1.5 μ as recited in a), is a low viscosity rubber having a solution viscosity (5 percent in styrene at 20°C) in the range 20 to 120 centipoise (cps) and a Mooney viscosity (ML+1, 100°C) of 30 to 80. Suitable rubbers include both so-called radial or star rubbers having three or more polymer segments bonded to a single polyfunctional element or compound, or a branched rubber having a
10 cis content of less than 75 percent and at least one, or a significant number of subordinate chains of sufficient length such that the viscosity of the rubber is less than the viscosity of a linear polymer of the same monomeric components and same molecular weight. Such rubbers useful in a), typically have a relatively high average molecular weight, a relatively low solution viscosity and a medium to high Mooney
15 viscosity. In general, the solution viscosity for the rubber will be below 120 cps while the Mooney viscosity will be less than 80 cps.

The radial or branched rubber preferably employed in a) of the present invention typically exhibits a second order transition temperature not higher than 0°C, and preferably not higher than -20°C. Suitable rubbers include alkadienes which include
20 1,3-conjugated dienes such as butadiene, isoprene, chloroprene or piperylene. Most preferred are homopolymers prepared from 1,3-conjugated dienes, with homopolymers of 1,3-butadiene being especially preferred. Alkadiene copolymer rubbers containing small amounts, for example up to 10 or 15 weight percent, of other monomers such as vinyl aromatics can also be employed if the rubbers meet the other qualifications
25 described herein.

Polymers having random branching, as well as methods for their preparation, are known in the art and reference is made thereto for the purpose of this invention. Representative branched rubbers and methods for their preparation are described in Great Britain Patent No. 1,130,485 and in *Macromolecules*, Vol. II, No. 5, pg. 8, by R. N.
30 Young and C. J. Fetters.

Radial or star polymers, commonly referred to as polymers having designed branching, are conventionally prepared using a polyfunctional coupling agent or a polyfunctional initiator. Methods for preparing star or radial polymers having designed branching are well-known in the art. Methods for preparing a polymer of butadiene
35 using a coupling agent are illustrated in US-A-4,183,877; US-A-4,340,690; US-A-4,340,691 and US-A-3,668,162, whereas methods for preparing a polymer of butadiene using a polyfunctional initiator are described in US-A-4,182,818; US-A-4,264,749; US-A-3,668,263 and US-A-3,787,510.

As known by those skilled in the art, various techniques such as control of the branching and molecular weight control can be used to adjust and tailor these polymers to achieve the necessary solution and Mooney viscosities, as well as the ratio of these two.

5 The rubber suitable for use to produce the rubber particles having a volume average particle size of 1.5 to 10 μ , as recited in b), can be the same rubber as described previously in a), a different rubber, or a mixture thereof. Typically the rubber can be any rubbery polymer which can be dissolved in the vinyl aromatic monomer. Preferred rubbery polymers include a homopolymer or copolymer of an alkadiene or a ethylene-
10 propylene copolymer optionally containing a non-conjugated diene. More preferably, the rubber is a homopolymer of a 1,3-conjugated diene such as butadiene, isoprene, piperylene, and chloroprene, or a copolymer of a conjugated diene with one or more vinyl aromatic monomers such as styrene; alpha, beta-ethylenically unsaturated nitriles such as acrylonitrile; and alpha-olefins such as ethylene or propylene. Most preferred
15 rubbers are homopolymers of 1,3-butadiene and block or random copolymers of at least 30, more preferably from 50 to 90, weight percent 1,3-butadiene and up to 70, more preferably from 5 to 50, weight percent of a vinyl aromatic compound, preferably styrene. The rubber utilized to produce large rubber particles of b) is preferably a polybutadiene. The rubber utilized to produce small rubber particles of a) is preferably
20 a star or branched polybutadiene or a poly(butadiene-styrene)block copolymer.

The small rubber particles of a) typically have a core-shell (single, major occlusion) or cellular (multiple, minor occlusions) morphology or mixture thereof. The large particles of b) typically have a cellular or similar multiple-occlusion morphology.

The amount of rubber initially dissolved in the vinyl aromatic monomer is
25 dependent on the desired concentration of the rubber in the final rubber-reinforced polymer product, the degree of conversion during polymerization and the viscosity of the solution. The rubber is typically used in amounts such that the rubber-reinforced polymer product contains from 2 to 20 percent, preferably from 3 to 17 percent, and more preferably from 3 to 15 weight percent rubber, based on the total weight of the
30 vinyl aromatic monomer and rubber components, expressed as rubber or rubber equivalent. The term "rubber" or "rubber equivalent" as used herein is intended to mean, for a rubber homopolymer, such as polybutadiene, simply the amount of rubber, and for a block copolymer, the amount of the copolymer made up from monomer which when homopolymerized forms a rubbery polymer, such as for a butadiene-styrene block
35 copolymer, the amount of the butadiene component of the block copolymer.

The polymerization is preferably conducted in one or more substantially linear stratified flow or so-called plug-flow type reactors, as described in UUS-A-2,727,884.

The techniques of mass-polymerization and the conditions needed for producing the desired average particle sizes are well known to one skilled in the art.

The temperature at which the polymerization is conducted will vary according to the specific components, particularly initiator, but will generally vary from 60 to 190°C.

5 The polymerization can be conducted in the presence of an initiator. Suitable initiators include any initiator capable of imparting the desired grafting of polymer to the rubber particle under the conditions of polymerization and accelerating the polymerization of the vinyl aromatic monomer. Representative initiators include peroxide initiators such as peresters, for example tertiary butyl peroxybenzoate and
10 tertiary butyl peroxyacetate, dibenzoyl peroxide, dilauroyl peroxide, 1,1-bis tertiarybutyl peroxy cyclohexane, 1-3-bis tertiarybutylperoxy-3,3,5-trimethyl cyclohexane, and di-cumyl peroxide. Photochemical initiation techniques can be employed if desired. Preferred initiators include dibenzoyl peroxide, tertiarybutylperoxy benzoate, 1,1-bistertiarybutylperoxy cyclohexane and tertiarybutylperoxy acetate.

15 Initiators may optionally be employed in a range of concentrations dependent on a variety of factors including the specific initiators employed, the desired levels of polymer grafting and the conditions at which the mass polymerization is conducted. Specifically, initiators may be employed in amounts from 0 to 2000, preferably from 100 to 1500, parts by weight per million parts by weight of vinyl aromatic monomer.

20 Additionally, a solvent may be used in the polymerization process. Acceptable solvents include normally liquid organic materials which form a solution with the rubber, vinyl aromatic monomer and the polymer prepared therefrom. Representative solvents include aromatic and substituted aromatic hydrocarbons such as benzene, ethylbenzene, toluene, xylene or the like; substituted or unsubstituted, straight or
25 branched chain saturated aliphatics of 5 or more carbon atoms, such as heptane, hexane, octane or the like; alicyclic or substituted alicyclic hydrocarbons having 5 or 6 carbon atoms, such as cyclohexane. Preferred solvents include substituted aromatics, with ethylbenzene and xylene being most preferred. In general, the solvent is employed in amounts sufficient to improve the processability and heat transfer during
30 polymerization. Such amounts will vary depending on the rubber, monomer and solvent employed, the process equipment and the desired degree of polymerization. If employed, the solvent is generally employed in an amount of up to 35 weight percent, preferably from 2 to 25 weight percent, based on the total weight of the solution.

35 Other materials may also be present in the polymerization process, including plasticizers, for example mineral oil; flow promoters, lubricants, antioxidants, catalysts, mold release agents, or polymerization aids such as chain transfer agents, including alkyl mercaptans, for example n-dodecyl mercaptan. If employed, a chain transfer agent

is typically present in an amount of from 0.001 to 0.5 weight percent based on the total weight of the polymerization mixture to which it is added.

Crosslinking of the rubber in the resulting product and removal of the unreacted monomers, as well as any solvent, if employed, and other volatile materials is
5 advantageously conducted employing conventional techniques, such as introducing the polymerization mixture into a devolatilizer, flashing off the monomer and other volatiles at elevated temperature, for example, from 200 to 300°C under vacuum and removing them from the devolatilizer.

In bimodal compositions, two distinct volume average particle sizes are
10 produced and combined. In particular, the rubber particles have different volume average particle sizes, wherein one contains small rubber particles having a volume average particle size of from 0.1 to 1.5 micrometers, and the other contains large rubber particles having a volume average particle size of from 1.5 to 10 micrometers, with the proviso that when the volume average particle size of the small particles is greater than
15 1 μ , the large particles have a volume average particle size of at least 2 μ .

In bimodal compositions, the desired ratio of the small to large particles is dependent upon the properties desired in the final rubber-reinforced polymer. Typically the amount of small particles ranges from 50 to 99, preferably from 75 to 96, and most preferably from 80 to 95 percent of the total amount of rubber particles in the rubber-
20 reinforced polymer. For products which require high gloss properties, the amount of small particles is from 85 to 98 percent and the amount of large particles is 2 to 15 percent. Other polymers in which higher impact strength is desirable can have 65 to 75 percent small particles and 25 to 35 percent large particles.

As used herein, the volume average particle size refers to the diameter of the
25 rubber particles, including all occlusions of vinyl aromatic polymer within the rubber particles. Volume average particle sizes and distributions may be measured using conventional techniques such as a Coulter CounterTM or, transmission electron microscopy image analysis. Large particles are measured using a 50 μ tube and smaller particles are measured by using a 20 micron tube.

In one embodiment of the present invention, a high impact polystyrene (HIPS)
30 composition is produced comprising a polymerized vinyl aromatic monomer, with dispersed particles of rubber having a bimodal particle size distribution. The size of the rubber particles are dependent upon the desired gloss and impact properties of the polymer product. For bimodal HIPS compositions, the small rubber particles are
35 typically in the range of from 0.1 to 1.5 μ , preferably from 0.2 to 1.3, more preferably from 0.3 to 1.2 and most preferably from 0.2 to 1.1 μ , and the large rubber particles are typically from 1.5 to 10, preferably from 1.8 to 8, more preferably from 1.8 to 7 and most preferably from 2.0 to 6 μ .

Alternatively, the process may be utilized in the preparation of acrylonitrile-butadiene-styrene (ABS) type compositions, in which an alkenyl nitrile, generally acrylonitrile is used as a comonomer. For bimodal ABS compositions the small particles are typically in the range of from 0.2 to 1, preferably from 0.3 to 1, more preferably from 0.4 to 0.9 and most preferably from 0.5 to 0.8 μ and the large rubber particles are typically from 1.5 to 10, preferably from 1.5 to 6, more preferably from 1.5 to 5 and most preferably from 1.5 to 4 μ .

Due to the excellent balance of gloss and toughness properties, these rubber-reinforced bimodal compositions are useful in a wide variety of applications such as consumer electronics, small household appliances, toys and furniture. These polymers are also useful in extrusion applications such as in the preparation of a gloss layer using coextrusion techniques for refrigerator liners.

The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and they should not be so interpreted. Amounts are in parts by weight unless otherwise indicated.

EXAMPLES

Two feeds, a) and b) are prepared for each Example as listed in Table 1.

The following rubbers are available from Bayer AG of Germany:

HX528, a polybutadiene rubber.

HX565, a low cis star branched rubber.

BL65533, a 60/40 butadiene/styrene block rubber.

200 kg of Feed was prepared as given in below table 1 and a) is fed to the top of a 2.5 liter agitated stirred tube reactor with a volume of 2.5 liters at the rate given in Table I. As the first polymerization feed travels down the reactor, the temperature of the polymerization is increased to maintain the rate of polymerization, typically from 112 to 130°C.

50 kg of Feed was prepared as given in table 1 and b) is fed to the top of a second agitated 1.1 liter stirred tube reactor. As the second polymerization feed travels down the reactor, the temperature of the polymerization is increased to maintain the rate of polymerization, typically from 120 to 135°C. The first and second reactors are operated to yield a solids content (polystyrene and rubber together) of 25 to 45 percent.

The partially polymerized mixture from each of the first and second reactors are then combined and fed into a third reactor identical to that used for Feed a). The third reactor is operated to yield a solids content of 50 to 70 percent. The partial polymer coming out of the third reactor is then fed into a fourth reactor wherein they are further polymerized to 70 to 90 percent solids and fed into a devolatilizing extruder to remove unreacted monomers and diluents. The resultant polymer melt is then cut with a rotating knife into granules.

TABLE I

Run No.	I*		II*		III		IV	
Feed	a	b	a	b	a	b	a	b
Rubber	PB	PB	BLOCK	PB	STAR-BRANCHED	PB	STAR-BRANCHED	PB
Wt. RUBBER (kg)	11.5	2.9	23	3.4	17	3.6	19.6	3.6
Wt. styrene(kg)	172.5	43.1	161	42.6	167	42.4	164.4	42.2
Wt. Ethylbenzene (kg)	12	3	12	3	12	3	12	3
Wt. mineral oil (kg)	4	1	4	1	4	1	4	1
wt. initiator (g)	64	0	0	0	70	0	50	0
wt. NDM (g)	0	5	0	7.5	0	32.5	0	24
feed rate (g/hr)	1200	150	900	110	1000	100	1020	140
final product rate (g/hr)	1114		804		887		959	

PB=Polybutadiene HX528

Block=Block copolymer rubber BL65533

Star-Branched=low cis star branched rubber HX565

5 Initiator is tertiary-butylperbenzoate

NDM=n-dodecyl mercaptan

*COMPARATIVE EXAMPLES

Feed rates are optimized for each run to produce product of optimum balance and gloss for the rubber used.

10 Tensile testing is done on an Instron Tensile machine, using a pulling speed of 5 mm/min. according to ASTM D-638.

Notched Izod Impact testing is also done on injection molded specimens according to ASTM test method D-256.

15 Charpy Impacts are determined using injection molded bars according to the test method ISO-179-2C.

Gloss measurements are done using two sets of molding conditions reflecting 1) molding conditions for optimized gloss and 2) molding conditions for optimized output or reduced cycle time to produce the molded part, on an Arburg All Rounder 170CM. Molding conditions for optimized gloss (1) are high mold temperature, high melt temperature and high injection speed. Molding conditions for optimized output (2) are those that lead to a low level of gloss, including low melt temperature, low mold temperature and low injection speed. The difference between the gloss measurements under both of these conditions generally reflect the gloss sensitivity of the material. A greater difference between the measurements indicates a more gloss sensitive product and vice versa. For high gloss applications a low gloss sensitivity is desired. Sixty degree Gardner measurements are done using a Dr. Lange device.

The following molding conditions are given for the two different gloss measurements.

TABLE II

	1)Optimized Gloss	2)Optimized Output
Temperature of Polymer melt (°C ¹)	250-230-210-190	210-200-190-180
Mold temp. (°C)	50	30
Injection Speed (cm ³ /min.)	45	10
Holding Pressure (bars) increased in steps of 50 bar	150 to 600	150 to 630
Sample Weight (g.)	6.65	6.65

- ¹Temperatures at four sites in the injection molding machine along the barrel representing molten polymer mass temperature. The first value is taken from the nozzle of the molding machine.

TABLE III
RESULTS

	I*	II*	III	IV
Rubber for a)	PB	BLOCK	Star Branched	Star Branched
Rubber for b)	PB	PB	PB	PB
Rubber for a) (wt. percent)	6.2	12.75	9.1	10.6
Rubber for b) (wt. percent)	0.77	0.93	0.9	1.07
Particle Size of a) particles (μ)	0.6	0.4	0.6	0.5
Particle Size of b) particles(μ)	3.2	3.9	5.6	5.1
Mineral Oil (wt. percent)	2.2	2.51	2.48	2.5
Physical Properties				
Melt Flow rate (g/10 min.)	9.8	8.1	5.5	6.7
Tensile Yield (MPA)	21	21	23	22
Tensile Rupture (MPA)	20	20	20	18
Elongation (percent)	48	38	37	33
Charpy Impact (kJ/m ²)	7.5	9.6	10.5	10.0
Izod Impact (J/m)	91	143	143	152
Good Gloss percent	88	93	87	91
Bad Gloss percent	33	58	64	65

PB=Polybutadiene HX528

Block=Block copolymer rubber BL65533

- 10 Star-Branched=low cis star branched rubber HX565

*COMPARATIVE EXAMPLES

Examples III and IV have high impact, excellent gloss and low gloss sensitivity. Thus excellent balance of impact and gloss is achieved without the use of expensive block copolymers.

CLAIMS:

1. A rubber modified monovinylidene aromatic polymer having a bimodal particle size distribution comprising:

- 5 a) rubber particles of a star or branched low viscosity rubber having a volume average particle size of from 0.1 to 1.5 μ , and cellular or core shell morphology or mixture thereof, and
- 10 b) rubber particles of a star or branched low viscosity rubber, linear diene rubber, or block copolymer rubber having a volume average particle size of from 1.5 to 10 μ , and a cellular morphology, with the proviso that when the volume average particle size of the particles of a) is greater than 1 μ , the volume average particle size of the particles of b) is at least 2 μ ,

wherein the particles of a) are from 50 to 99 wt. percent of the total diene rubber content.

15 2. The composition of Claim 1 wherein the rubber of a) is a homopolymer of butadiene.

3. The composition of Claim 1 wherein the rubber of b) is a homopolymer of butadiene.

20 4. The composition of Claim 1 wherein the polymer is a HIPS polymer and the rubber particles of a) are from 0.2 to 1.3 μ .

5. The composition of Claim 4 wherein the rubber particles of a) are from 0.3 to 1.2 μ

6. The composition of Claim 5 wherein the rubber particles of a) are from 0.2 to 1.1 μ .

25 7. The composition of Claim 1 wherein the polymer is a HIPS polymer and the rubber particles of b) are from 1.8 to 8 μ .

8. The composition of Claim 7 wherein the rubber particles of b) are from 1.8 to 7 μ .

30 9. The composition of Claim 8 wherein the rubber particles of b) are from 2 to 6 μ .

10. The composition of Claim 1 wherein the polymer is an ABS polymer and the rubber particles of a) are from 0.2 to 1 μ .

11. The composition of Claim 10 wherein the rubber particles of a) are from 0.3 to 1 μ .

35 12. The composition of Claim 11 wherein the rubber particles of a) are from 0.4 to 0.9 μ .

13. The composition of Claim 12 wherein the rubber particles of a) are from 0.5 to 0.8 μ .

14. The composition of Claim 1 wherein the polymer is an ABS polymer and the rubber particles of b) are from 1.5 to 10 μ .
15. The composition of Claim 14 wherein the rubber particles of b) are from 1.5 to 6 μ .
- 5 16. The composition of Claim 15 wherein the rubber particles of b) are from 1.5 to 5 μ .
17. The composition of Claim 16 wherein the rubber particles of b) are from 1.5 to 4 μ .
- 10 18. The composition of Claim 1 wherein the rubber particles of a) have a core shell morphology.
19. The composition of Claim 1 wherein the rubber particles of a) have a cellular morphology.
20. The composition of Claim 1 wherein the rubber particles of a) have a mixture of core shell and cellular morphology.
- 15 21. The composition of Claim 1 wherein the polymer is a HIPS polymer wherein the volume average particle size of the particles of a) is from 0.3 to 0.8 μ and the volume average particle size of the particles of b) is from 5 to 6 μ .
22. Articles produced from the composition of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/16501

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F279/02 C08F287/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 418 042 A (DOW CHEMICAL CO) 20 March 1991 see abstract see page 3, line 12 - line 16 see page 3, line 27 - line 33 see page 3, line 44 - line 46 see page 3, line 56 - line 58 see page 4, line 7 - line 11 see page 4, line 47 - line 48 see page 9, line 1 - line 8 see tables 1,2	1-9, 18-20,22
A	see claims --- -/--	1-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 December 1998

Date of mailing of the international search report

10/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Pollio, M

INTERNATIONAL SEARCH REPORT

Int'l. Application No.

PCT/US 98/16501

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 0 832 904 A (ENICHEM SPA) 1 April 1998 see abstract see page 3, line 56 - line 58 see page 5, line 2 - line 4 see example 5	1-9,22
A	see claims 1,4,5,7-9 ---	1-22
Y	EP 0 412 801 A (DOW CHEMICAL CO) 13 February 1991 see abstract see page 3, line 41 - line 43 see page 4, line 11 - line 23 see page 6, line 57 - page 7, line 16 see tables see claims	1-22
Y	EP 0 732 345 A (ENICHEM SPA) 18 September 1996 see abstract see examples 4-7 see tables see claims 1-9 ---	1-22
A	EP 0 277 687 A (DOW CHEMICAL CO) 10 August 1988 cited in the application see abstract see claims see page 5, line 9 - line 53 see page 6, line 30 - line 49 see page 8, line 4 - line 10 see page 8, line 36 - line 43 see tables -----	1-22



INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte lonal Application No

PCT/US 98/16501

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0418042 A	20-03-1991	AU 629036 B AU 6237990 A CA 2025097 A DE 69006667 D DE 69006667 T ES 2062393 T JP 3119013 A US 5179166 A US 5264492 A	24-09-1992 21-03-1991 13-03-1991 24-03-1994 12-01-1995 16-12-1994 21-05-1991 12-01-1993 23-11-1993
EP 0832904 A	01-04-1998	IT MI961978 A JP 10130343 A	27-03-1998 19-05-1998
EP 0412801 A	13-02-1991	AU 624015 B AU 6029590 A CA 2022925 A DE 69008971 D DE 69008971 T ES 2053116 T HK 80094 A JP 3103414 A SG 95394 G US 5240993 A	28-05-1992 14-02-1991 10-02-1991 23-06-1994 01-09-1994 16-07-1994 19-08-1994 30-04-1991 28-10-1994 31-08-1993
EP 0732345 A	18-09-1996	IT MI950505 A	16-09-1996
EP 0277687 A	10-08-1988	NL 8700208 A AU 606645 B AU 1032188 A CA 1307865 A DE 3889555 D DE 3889555 T JP 63248809 A KR 9600567 B	16-08-1988 14-02-1991 04-08-1988 22-09-1992 23-06-1994 01-09-1994 17-10-1988 09-01-1996